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(54) **PRODUCTION OF FERROUS SULFATE OR IRON POLYSULFATE HAVING HIGH PURITY FROM WASTE HYDROCHLORIC ACID CONTAINING FERROUS COMPOUND**

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a process for producing an iron polysulfate having sufficiently high purity to enable the use as a flocculant for city water supply and ferrous sulfate having high purity and useful as a precursor of the polysulfate from waste hydrochloric acid containing a large amount of a ferrous compound and discharged from a pickling step, etc.
SOLUTION: A waste hydrochloric acid solution containing a large amount of a ferrous compound such as waste liquid of pickling process is concentrated by evaporation and the produced saturated solution is cooled at a cooling rate of 3-5[deg]C/h to effect the crystallization and separation of ferrous chloride. The obtained ferrous chloride is mixed with sulfuric acid, the mixture is concentrated by evaporation to obtain a, concentrated solution of ferrous sulfate, ferrous sulfate crystal is crystallized and separated from the concentrated solution and the obtained ferrous sulfate is oxidized to obtain an iron polysulfate.

CLAIMS

[Claim(s)]
[Claim 1]A process of preparing a saturated solution from hydrochloric acid waste liquid containing a lot of ferrous compounds and a little heavy metal compounds, A manufacturing method of high grade ferrous sulfate which consists a process of cooling a saturated solution, carrying out evaporation concentration of the ferrous chloride after mixing sulfuric acid to crystallization, a process to separate, and obtained ferrous chloride, and preparing a strong solution of ferrous sulfate, and this strong solution to a ferrous sulfate crystal of crystallization and a process to separate.
[Claim 2]A process of preparing a saturated solution from hydrochloric acid waste liquid containing a lot of ferrous compounds and a little heavy metal compounds, A process of cooling a saturated solution, carrying out evaporation concentration of the ferrous chloride after mixing sulfuric acid to crystallization, a process to separate, and obtained ferrous chloride, and preparing a strong solution of ferrous sulfate, A manufacturing method of high grade polyferrous sulfate which consists of a process of oxidizing crystallization, a process to separate, and obtained ferrous sulfate in a ferrous sulfate crystal from this strong solution, and manufacturing polyferrous sulfate.
[Claim 3]The manufacturing method according to claim 1 or 2 which carries out a cooling rate for ferrous chloride in h and 3-5 ** /in crystallization and a process to separate.
[Claim 4]The manufacturing method according to claim 1, 2, or 3 which prepares a saturated solution by decompression evaporation concentration at temperature of 50-70 ** in a process of preparing a saturated solution, from hydrochloric acid waste liquid.
[Claim 5]Claims 1, 2 and 3 which condense evaporating hydrogen chloride gas in a process of preparing a strong solution of ferrous sulfate, and make chlorides collect, and a manufacturing method given in four.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the technology of manufacturing ferrous sulfate of the high grade which are polyferrous sulfate of a high grade, and its precursor from the hydrochloric acid waste liquid containing a lot of ferrous compounds, such as pickling abraum salt acid discharged by steel relations, and a little heavy metal compounds.
[0002]
[Description of the Prior Art]About the hydrochloric acid waste liquid which contains ferrous compounds, such as this pickling abraum salt acid, so much. How to carry out sea dumping after being unable to abandon as it is, but neutralizing and considering it as sludge since water pollution will be caused, Or about the generated ferrous sulfate, the method of using that part as a flocculating agent, etc. are already known at the same time it collects chlorides by a distillation-under-reduced-pressure method, after adding sulfuric acid in this abraum salt acid.
[0003]
[Problem to be solved by the invention]Among these conventional technologies, considering the point of carrying out sea dumping, about processing by the former method, it is not desirable and substitution to more advanced waste treatment

technology is desired. Although complete treatment is performed about the latter method as compared with the former and it is desirable, there are few uses of the produced ferrous sulfate, as a result, use is restricted in part, and adoption of this technology is not progressing so that it may consider.
[0004]Then, the thing which this invention persons make the purity of the ferrous sulfate produced improve, as a result of reaching Conclusion that use of this product is urged in more fields, a use is expanded as a result and the complete treatment of abraum salt acid is urged and furthering research and development, the technology of manufacturing high grade ferrous sulfate which is polyferrous sulfate of a high grade and its precursor from the first iron compound salt acid waste of ** is completed. That is, if it puts in another way, an object of the invention in this application will be to manufacture ferrous sulfate which is polyferrous sulfate of a high grade, and its precursor, so that it is usable also as a flocculating agent of a water supply system from the hydrochloric acid waste liquid containing a lot of ferrous compounds and a little heavy metal compounds. This method also has the advantage that a product can be provided inexpensive, from using waste as starting material. Since it is as above, polyferrous sulfate which is a final product, It is possible to use it instead of aluminium compounds, such as aluminum sulfate currently used as a flocculating agent of the water supply system in Japan, The technology [it is inexpensive in the use of Al ion which the opinion of being a causative agent of Alzheimer these days also has, and] which can be avoided by using polyferrous sulfate of a high grade is provided.
[0005]
[Means for solving problem]It is what manufactures ferrous sulfate of a high grade, or polyferrous sulfate of a high grade in this invention from the hydrochloric acid waste liquid containing a lot of [as mentioned above] ferrous compounds and a small amount of heavy metals, Hydrochloric acid waste liquid is made to once generate ferrous chloride, and, subsequently to ferrous sulfate, this is made to change into it to having added sulfuric acid promptly and having produced ferrous sulfate at the invention in this application in conventional technology. And since the ferrous chloride obtained on that occasion becomes a thing of a high grade, it compares, when sulfuric acid is directly added in waste fluid and ferrous sulfate is manufactured, and in the invention in this application, it will become a high grade, and the produced ferrous sulfate finds out these facts, and completes this invention.
[0006]That is, in the invention in this application, the 50-70 ** saturated solution of ferrous chloride can be variously prepared under the chloride existence of concentration by evaporation concentration etc. from the hydrochloric acid waste liquid containing a lot of ferrous compounds and a small amount of heavy metals, by cooling this, ferrous chloride is crystallized and it is separated. In the invention in this application, by doing in this way, this invention persons find out that the ferrous chloride crystal of a high grade is obtained, and when the example of the crystallization is shown, it is as follows.

1) 98 kg of ferrous chloride crystals obtained by cooling the saturated solution of the temperature of 60 **, and 4% of the hydrochloric acid concentration of isolation which obtained the waste fluid 1t by carrying out evaporation concentration at 20 **.
2) 125 kg of ferrous chloride crystals obtained by cooling the saturated solution of the temperature of 60 **, and 10% of the hydrochloric acid concentration of isolation which obtained the waste fluid 1t by carrying out evaporation concentration at 20 **.
Subsequently, by mixing high-concentration sulfuric acid to this ferrous chloride, and forming and carrying out vacuum concentration of the ferrous sulfate to it, the ferrous sulfate which carried out crystallization is separated from a mother liquor, and then it oxidizes, and is considered as polyferrous sulfate. And when this whole process is illustrated, it is as drawing 1.

[0007]
[Mode for carrying out the invention]The abraum salt acid made into a processing object by this invention is discharged from the pickling process in iron manufacture, a wire production factory, or the apparatus factory of special steel stock, and there is pickling abraum salt acid mentioned above, for example in it. And when invention-in-this-application persons analyzed iron content about the pickling abraum salt acid (as Fe2+), it was about 50-100 g/l. In the invention in this application, it is the first process and the saturated solution or ********** (in the description of the claim for patent clause, a "saturated solution" is used in the sense of both) of ferrous chloride is prepared from the chloride raw material waste fluid which contains this ferrous compound so much first.
[0008]Evaporation concentration performs preparation of a saturated solution. Although it is desirable in that case that it is perfect saturation, it is not what is restricted to it, In the following crystallizing process, ferrous chloride crystallizes, and if it is the concentration which is a grade which can acquire the quantity which is a grade which does not interfere practically, it is sufficient (in addition, the above mentioned "**********" calls the solution in a ****** state in such the state, i.e., perfect saturation). Although a pressure can carry out heating evaporation at 90 - 760mmHg and the temperature of about about 50-100 **, it is preferred to carry out at the pressure 150 - 185mmHg, and 60 to 65 temperature. This is because separation with early iron and an impurity will worsen if it becomes the temperature with few impurities which is because ferrous chloride of a high grade is obtained more, and exceeded this range by choosing it as this range. As for the condensation, although the hydrogen chloride water content steam furthermore generated in that case is condensed and chloride is made to form, it is preferred to adopt the surface condenser which uses cooling fluid about 40 ** or less.
[0009]Cooling performs a deposit of the crystal in the crystallizing process following a saturated solution preparation process. As for the temperature which makes cooling end in that case, near ordinary temperature is practical. The range of 3-5 **/h is desirably [it is important to control a cooling rate and / carrying out in h and 1-10 ** /], and more preferably good. By this control, it can avoid going together into the ferrous chloride in which heavy metals contained in raw material waste fluid, such as Mn and Cr, were manufactured, and ferrous chloride of a high grade is obtained in it. That is, it can decrease or less [of the ratio at the time of the ratio of the heavy metal which exists during the manufactured ferrous chloride crystal by this control existing in raw material waste fluid] to 1/10. If especially a cooling rate is made into the range of 3-5 **, this ratio can decrease or less to 1/100. Although explained repeatedly, it is the greatest feature of the invention in this application to have adopted this process, and ferrous sulfate of a high grade or polyferrous sulfate of a high grade can be manufactured by existence of this process.

[0010]It can control going together during the ferrous chloride crystal which generated heavy metals contained in raw material waste fluid, such as Mn and Cr, by choosing the conditions of this process, especially a cooling rate like the point. The crystal which the content ratio of a heavy metal can be most reduced if it limits to the range which described especially the cooling rate above, and is easy to separate from a mother liquor by this control can be formed simultaneously. Although various solid-liquid-separation machines, such as a centrifuge, can be used for separation of the formed ferrous chloride crystal, it is preferred to adopt a pars-basilaris-ossis-occipitalis discharge type centrifuge.
[0011]In the process which mixes sulfuric acid to ferrous chloride and in which ferrous sulfate is made to form of following a crystallizing process, dissolve ferrous chloride in water first and about 38weight % of solution is made to form, sulfuric acid is added to this, it adjusts to 35 to 65 weight % of isolation sulfuric acid concentration, and ferrous sulfate is formed. Subsequently,

although evaporation concentration of this is carried out, it is 60-65 ** in temperature, and it is preferred to carry out under the pressure of about 150-185 mmHg. The concentration of sulfuric acid has [the solution obtained after the end of concentration / the 40 weight % order] the preferred concentration of ferrous sulfate just over or below 25 weight % (as FeSO4).

[0012]The process of carrying out crystallization of the formed ferrous sulfate is performed by cooling the condensed ferrous sulfate content mother liquor. As for cooling, it is desirable that you make it fall from 60-65 ** at the time of concentration near ordinary temperature and to around 20 ** of ******. The cooling rate in that case is desirable in about 5 **/h, when it takes into consideration forming the good crystal of a filtration efficiency. As for the precipitated crystal, it is efficient to be based on a pars-basilaris-ossis-occipitalis discharge type centrifuge with various kinds of solid-liquid-separation machines, although it is disengageable, and it is desirable.

[0013]The process of manufacturing polyferrous sulfate following the process of carrying out crystallization of the ferrous sulfate dissolves ferrous sulfate in water first, generates the solution, and it mixes concentrated sulfuric acid so that it may become this subsequently to SO4/Fe=1.0 - 1.5. The amount of the water used in the case of solution formation is about 1800 ml per kg of FeSO4 crystal (FeSO4-H20). When the ratio of SO4/Fe of the manufactured ferrous sulfate is in this range, it is not necessary to use concentrated sulfuric acid. Then, polyferrous sulfate which is the last object will be manufactured by oxidizing this. Although an oxidizer in particular is not limited, oxygen or hydrogen peroxide is preferred, and it is preferred to make a catalyst exist in that case. Although the oxidation reaction catalyst for an aquosity reaction is usable for a catalyst, nitrogen oxides etc. are preferred, for example.

[0014]

[Working example]The embodiment which manufactures polyferrous sulfate of a high grade and its precursor for 2000 kg of pickling abraum salt acid discharged from the surface treatment process of an iron mill as a raw material of waste fluid is shown below. When this waste fluid was analyzed, that presentation was as in Table 1. Subsequently, it maintained to the temperature of 60-65 **, the pressure 150 - 185mmHg, vacuum concentration was performed, and the saturated solution of ferrous chloride was formed. The obtained saturated solution was cooled to 20 ** with the cooling rate at 3 **/h, the crystal of ferrous chloride was deposited, subsequently the pars-basilaris-ossis-occipitalis discharge type centrifuge separated the crystal, and crystal FeCl2 and 4H20188kg of ferrous chloride was obtained. When the ingredient of the obtained crystal was analyzed, it became a result as shown in Table 2.

[0015]

[Table 1]

原料廃液の組成

含有成分	T-Fe (Fe^{2+})	T-Cl	Mn	Cr	Ni	W	Mo	Cu
含有量(g/l)	188	258	1.06	0.5	0.056	0.035	0.021	0.017

比重：1．３３２

ＦｅＣｌ$_2$として含有量３２重量%

ＦｒｅｅのＨＣｌ　1．４重量%

[0016]
[Table 2]
製造された塩化第一鉄の組成

	Fe	Cl	Mn	Cr	Ni	W	Mo	Cu
$FeCl_2$ 結晶 $FeCl_2$ $4H_2O$(重%)	34.0	35.7	0.002	0.001	ND	ND	ND	ND
$FeCl_2$ 溶解液	188 g/l	198 g/l	11 mg/l	5.5 mg/l	ND	ND	ND	ND

[0017]Both tables are compared and the abundance of Mn under raw material waste fluid and manufactured crystal is seen. First, when Mn/Fe in raw material waste fluid is calculated, it turns out that it is set to 0.0056 and is decreasing to 100 by about 1/as the crystal as compared with Mn/Fe [in / for this / a crystal] (0.000058). When it compares similarly about Cr, it turns out that it is decreasing to 100 by about 1/. It turns out that the content ratio of the heavy metal component contained in very small quantities can be decreased if raw material waste fluid to a ferrous chloride crystal is deposited from these things, and ferrous chloride of a high grade can be manufactured. And the thing of more desirable purity is obtained by managing [h] the cooling rate at the time of crystallization in 3-5 ** /in that case.
[0018]188 kg of obtained ferrous chloride crystals were dissolved in water, it adjusted so that sulfuric acid might be added to this and it might become 65% of total sulfuric acid concentration, and 688 kg of adjustment liquid was obtained. Evaporation concentration was carried out at the pressure 150 - 185mmHg, and the temperature of 60-65 **. The obtained concentrated solution was cooled to 20 **, it deposited, the crystal of ferrous sulfate was centrifuged with the pars-basilaris-ossis-occipitalis discharge type centrifuge, and ferrous sulfate crystal FeSO4 and H2O153.1kg were obtained. The cooling rate in that case was carried out in h and 5 ** /. When the ingredient of the obtained crystal was analyzed, it was as in Table 3.
[0019]
[Table 3]
製造された硫酸第一鉄の組成

	Fe	SO_4	Cl	Mn	Cr
$FeSO_4$ 結晶 $FeSO_4$ $7H_2O$(重%)	20.1	34.6	ND	0.0002	0.0001

[0020]153.1 kg of crystals (FeSO4-H2O) of the ferrous sulfate obtained here were dissolved in 275.6 kg of water. 29.2 kg of concentrated sulfuric acid (98%) was added so that it might be set to SO4/Fe=1.325 to this. Subsequently, it oxidized, polyferrous sulfate was manufactured and 458 kg was obtained. On that occasion,

the oxidizer used 7.20 kg O2, using nitrogen oxides as a catalyst. When the ingredient of the manufactured polyferrous sulfate was analyzed, it became a presentation as shown in Table 4. In this table, the presentation of the polyferrous sulfate manufactured with the conventional method (namely, method of manufacturing ferrous sulfate, without passing through the process of manufacturing ferrous chloride from waste fluid) was also doubled and written.

[0021]
[Table 4]

実施例及び従来法によりそれぞれ製造されたポリ硫酸鉄の組成

	T-Fe (Fe^{3+})g/l	SO_4 g/l	Cl	Mn mg/l	Cr mg/l	Ni mg/l	W mg/l	Mo mg/l	Cu mg/l
実施例	160	365	ND	1	1	ND	ND	ND	ND
従来法	160	365	ND	1181	373	28	ND	ND	6

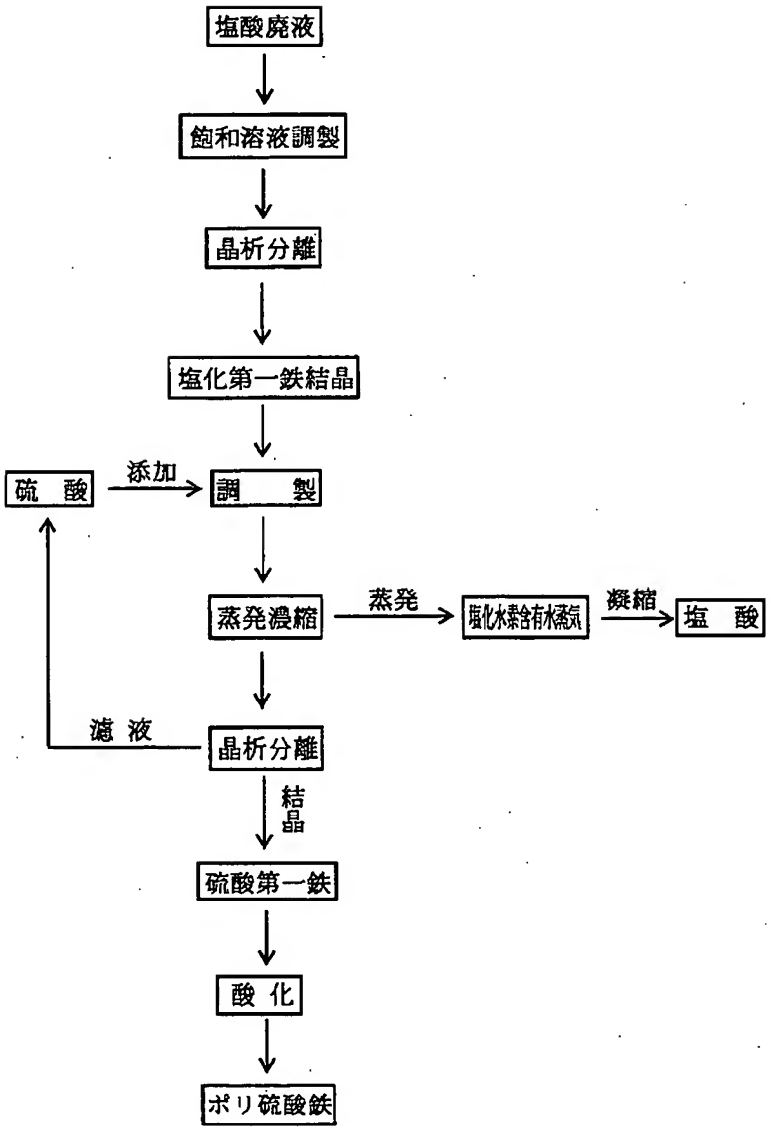
[0022]
[Effect of the Invention]In this invention, from the hydrochloric acid waste liquid containing a lot of ferrous compounds and a small amount of heavy metals, ferrous sulfate which is polyferrous sulfate of a high grade and its precursor is manufactured so that it is usable also as a flocculating agent of a water supply system, but it can do. This manufacturing method also has the advantage that polyferrous sulfate can be provided inexpensive, from using waste as starting material. As a result, use of the polyferrous sulfate manufactured from waste in more fields can be urged, as a result, a use can be expanded, and the spreading and promotion of the treatment technique of abraum salt acid which perform not low-level waste treatment but the complete treatment called ocean dumping etc. can be expected. It is possible to use it in Japan instead of aluminium compounds, such as aluminum sulfate currently used for the present large quantity as a flocculating agent of a water supply system, furthermore, The technology it becomes possible to avoid use with the water supply system of an aluminium compound which the opinion of being a causative agent of Alzheimer these days also has as a result is also provided.
[0023]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is a flow chart of this invention and the process from the concentration step of hydrochloric acid waste liquid to the polyferrous sulfate acquisition which is the last object is shown.

DRAWINGS

[Drawing 1]


塩酸廃液
飽和溶液調製
晶析分離
塩化第一鉄結晶
硫　酸
添加
調　　製
蒸発濃縮
蒸発
塩化水素含有水蒸気
凝縮
塩　酸
濾 液
晶析分離
結晶
硫酸第一鉄
酸 化
ポリ硫酸鉄